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Development of a continuous measurement system of PANs and alkyl nitrates in the atmosphere and observations at Suzu, th

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Peroxyacyl nitrates (PANs) and alkyl nitrates (ANs) are generated in the atmosphere by oxidation of NO_x in the presence of solar ultraviolet. They have a comparatively long lifetime, and are important as transboundary air pollutants. On the other hand, PANs and ANs act as the reservoirs of NO_x. In order to clarify transboundary pollution of nitrogen oxides, comprehensive measurements of total odd nitrogen species (NO_y), including PANs and ANs, are required. In this research, a continuous measurement system of total PANs and ANs has been developed by a thermal dissociation / cavity attenuated phase shift spectroscopy (TD/CAPS) method.

This instrument consists of heated quartz tubes to decompose PANs and ANs into NO_2, and a CAPS-NO_2 analyzer. This system has three intake lines; NO_2, PANs and ANs lines. The NO_2 line equip of a quartz tube without heating. The PANs and ANs line equip quartz tubes heated at 433 K and 633 K, respectively for thermally decomposing them into NO_2. Concentrations of NO_2, NO_2 + PANs and NO_2 + PANs + ANs can be obtained from the NO_2, PANs and ANs lines, respectively. These concentrations are sequentially measured by switching solenoid valves and then NO_2, PANs and ANs concentrations are obtained. Since a part of HNO_3 is pyrolyzed in the ANs line, annular denuder coated with NaCl to remove HNO_3 is set before the heated quartz tube in the ANs line. The decomposition efficiencies of PANs and ANs were calibrated to be 100 and 95%, respectively, for all kinds of PANs and ANs examined.

Continuous field observations of PANs and ANs have been being performed at NOTOGRO (Noto ground-based Research observatory) supersite in Suzu, the Noto Peninsula, since November 2012. Continuous measurements of NO_x, NO_y, T.NO_3 (the sum of gaseous nitric acid and particulate nitrate) O_3, and CO have also been being conducted. NO_y concentrations were in agreement with the sum of observed NO_y components (= NO_x + T.NO_3 + PANs + ANs) regardless of seasons. NO_x fractions were the highest in NO_y constituents. Fractions of T.NO_3 in January and February were lower than those in other months. This reflects that wet deposition of T.NO_3 would be accelerated in winter due to snowfall. On the other hand, PANs fractions in spring and summer were smaller than those in winter. This suggests that temperature increasing promotes decomposition of PANs.

Keywords: peroxyacyl nitrates (PANs), alkyl nitrates, total odd nitrogen species, cavity attenuated phase shift spectroscopy